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A method for calculating the liquid density for the CO_2-H_2O-NaCl system under CO_2 storage condition

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Abstract

A liquid density model for the H_2O-CO_2-NaCl ternary system is established, based on previous methods (Duan et al. *Energy & Fuels* 2008, 22, 1666-1674), and combined with a recent density model for H_2O-NaCl binary solution (Mao and Duan. *The Journal of Chemical Thermodynamics* 2008, 40, 1046-1063). The applicable range of the model is 273-573 K, 0.001-1000 bar and 0-6 mol/kg NaCl concentration as well as CO_2 concentrations from 0 up to saturated conditions. The model is accurate and its total error is within 0.5%. The applicable range totally covers conditions for geological storage of CO_2. Therefore it is suited for simulation studies of CO_2 geological storage, especially for fluid convection processes due to density differences. In order to facilitate the model application, a Matlab© program is provided which can be downloaded from our web page. Three examples are presented to demonstrate the model application. The first one is the calculation of pure water density varying with pressure at different temperature conditions. Second application is on the fluid density calculation under different CO_2 saturations which is relevant for convection process simulation. The last application shows the total pressure change caused by temperature changes under isometric conditions.

Keywords: CO_2,; OpenGeoSys; CCS; saline aquifers, liquid density

1. Introduction

CO_2 containing brine, especial the ternary H_2O-NaCl-CO_2 aqueous solution, is a geological fluid which is present in many subsurface environments. It is especially important in the case of geological storage of carbon dioxide in saline formations, as it then forms the reservoir fluid [1]. The fluid properties influence the hydraulic processes, e.g.

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via density or viscosity, as well as the geochemical processes, e.g. via activity coefficients and solution contents. The density of this ternary fluid is a volumetric property and its accurate knowledge is fundamental in the quantitative interpretation of the above processes [2]. This knowledge is also very important in many industrial processes, such as the production of oil and gas, enhanced oil and gas recovery, geothermal exploitation, natural gas clathrate engineering, the treatment of exhaust gases, wastewater and waste liquids, supercritical fluid extraction and oxidation, fertilizers, hydrometallurgy, and seawater desalination [3-7]. Equations of state (EOS) for CO_2 have been proposed by [8], Peng-Robinson type EOS for the ternary H_2O-NaCl-CO_2 system were proposed by [9] or [10]. These equations have been widely used for CO_2 storage simulations (e.g. [11]).

This paper therefore provides a calculation method for determining the density of the ternary H_2O-NaCl-CO_2 aqueous solution in the range of 1-1000 bar, 273-573 K and 0-6 mol NaCl as well as 0 to saturated CO_2 concentration. The method is based on the work of [12] and offers improvements in terms of calculation efficiency and usability. In future work, this method will be extended to cover also the viscosity of the considered system.

2. Method

For the calculation of many thermodynamic properties, a molar volume model expressed in terms of pressure P [bar], temperature T [K] and molar fraction x is more convenient than a density model with the same independent variables [13]. The change of molar volume of a geological formation fluid due to the dissolution of CO_2 is usually far smaller than the molar volume of pure water, so the dissolution can be treated as a perturbation of the pure water volume. The volume of fluid containing CO_2 can thus be described by [12, 14].

$$V = V_1(1 + Kx_2) \tag{1}$$

where V [L³] is the volume of solution, V_1 [L³] is the molar volume of pure water and x_2 is the molar fraction of CO_2. In this paper, we employ the IAPWS-IF97 equations [15] to calculate the density of pure water. The coefficient K in eq. (1) is a function of temperature and pressure and can be approximated by [12].

$$K = a_1T^2 + a_2T + a_3 + a_4T^{-1} + a_5T^{-2} + \left(a_6T^2 + a_7T + a_8 + a_9T^{-1} + a_{10}T^{-2}\right)P \tag{2}$$

where T and P indicate temperature [K] and pressure [bar] and a_1-a_{10} are parameters listed in Table 1.

Table 1 Parameters a_1 through a_{10} for eq.(2) [12]

a_1	$0.38384020 \cdot 10^{-3}$
a_2	-0.55953850
a_3	$0.30429268 \cdot 10^{3}$
a_4	$-0.72044305 \cdot 10^{5}$
a_5	$0.63003388 \cdot 10^{7}$
a_6	$-0.57709332 \cdot 10^{-6}$
a_7	$0.82764653 \cdot 10^{-3}$
a_8	-0.43813556
a_9	$0.10144907 \cdot 10^{3}$
a_{10}	$-0.86777045 \cdot 10^{4}$

From eq. (1) the apparent molar volume of CO_2, $V_{\varphi,2}$, can be obtained:

$$V_{\varphi,2} = \left(V - x_1V_1\right) / x_2 = V_1\left(1 + K\right) \tag{3}$$

where x_1 and x_2 are the molar fraction of water and CO_2 respectively. The total volume V of the fluid can also be written as:

$$V = V_1x_1 + V_{\varphi,2}x_2 \tag{4}$$

The CO_2-H_2O-NaCl system is obtained by adding CO_2 to the H_2O-NaCl system, treating the H_2O-NaCl system as a hypothetical pure component (solvent). Following the Duan model [12], the sum of the apparent molar volumes is used to expand to the ternary system:

$$V = V_1 x_1 + V_{\varphi,3} x_3 + V_{\varphi,2} x_2 \tag{5}$$

where x_3 is the NaCl molar fraction and $V_{\varphi,3}$ is its apparent molar volume, which can be obtained from the model of [16]. Treating brine as a hypothetical component, the binary density model of [17] is used to work out the molar volume of the total fluid directly.

$$V = V_B x_B + V_{\varphi,2} x_2 \tag{6}$$

Here the subscript B indicates the H_2O-NaCl binary system. So V_B is the molar volume and x_B is the molar fraction, which is given by the sum of the molar fractions of water and NaCl. Using molalities of NaCl and CO_2, m_{NaCl} and m_{CO2}, as input conditions, we work out the following eq. (7)-(10) for calculation of eq. (6).

$$V_B = \frac{1000 + m_{NaCl} \cdot 58.4428}{\rho_B \cdot (55.51 + m_{NaCl})} \tag{7}$$

$$V_{\varphi,2} = \frac{1000 \cdot (1 + K)}{\rho_W \cdot 55.51} \tag{8}$$

$$x_B = \frac{55.51 + m_{NaCl}}{55.51 + m_{NaCl} + m_{CO2}} \tag{9}$$

$$x_2 = \frac{m_{CO2}}{55.51 + m_{NaCl} + m_{CO2}} \tag{10}$$

We used the density model of [12] to calculate the molar volume of pure water and aqueous NaCl solution and work out the density of the CO_2 brine fluid, eq. (11).

$$\rho = (1000 + 58.4428 \cdot m_{NaCl} + 44.0098 \cdot m_{CO2}) \Big/ \left(\frac{1000 + 58.4428 \cdot m_{NaCl}}{\rho_B} + \frac{18.0153 \cdot (1 + K) \cdot m_{CO2}}{\rho_W} \right) \tag{11}$$

Where ρ_B and ρ_W [g/cm^3] are densities of aqueous NaCl solution and pure water, respectively. Coefficient K is worked out by eq. (2) and m_{NaCl} and m_{CO2} are molalities of NaCl and CO_2 in solution, respectively. Finally we can obtain the density of the ternary solution, ρ [g/cm^3].

3. Implementation

Based on the above model, we implemented a dynamic link library in C/C++ to efficiently calculate the density of the fluid. This library and the source code are introduced in the open source scientific software OpenGeoSys [18-20]. The library has to be referenced providing the parameters temperature, pressure, molality of NaCl and molality of CO_2. For test and verification purposes, also a Matlab interface has been constructed.

The code tests the input values for consistency with the implemented theory and returns an error tag of -1 if the input values are out of the range of the code. Although the program does not limit the concentration of CO_2, it has to be ensured that the molality of CO_2 is consistent with the solubility at the given P and T conditions [21, 22]. The ranges covered by the method presented are 273.15-573.15 K, 0.001-1000 bar, 0-6 mol NaCl per kg and > 0 mol CO_2 per kg. If the input pressure is lower than the saturation pressure of pure water, the water is in the vapor phase. In this case, the program returns the density of pure water vapor, regardless of the molalities of NaCl and CO_2.

As a common international standard, the IF97 [15] has been widely used and verified for density calculations of pure water. Based on IF97, we obtain the density model for the H_2O-NaCl binary system. Due to the large amount of

available experimental data, an error of less than 0.05% can be assumed [17]. Furthermore, the H_2O-NaCl-CO_2 ternary system model has been tested with an average deviation of 0.25% and a maximum deviation of 2.8% [12, 23]. So the total error of the model is within 0.5%.

The code was tested for efficiency by calculating the density of the liquid phase for a range of pressure and temperature conditions. It was found, that the average execution time per density simulation is $5.0 \cdot 10^{-4}$ s on Intel© 2.66 GHz platform.

4. Verification and application

The density of pure water was calculated for two temperature conditions, 298.15 K and 338.15 K, varying pressure from 1 to 1000 bar. The results of the calculations are shown in Fig. 1, in comparison with standard reference data from NIST and the original IF97 program in C++ code. The results show a good agreement of the newly implemented code with prior results.

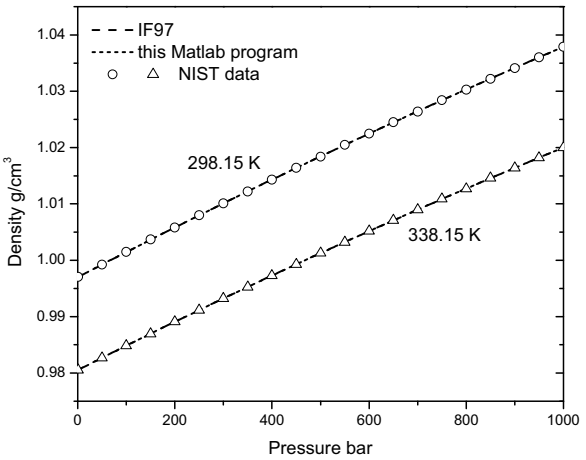

Figure 1. Calculated density of pure water varying with pressure at temperatures of 298.15 K and 338.15 K, compared to NIST data [24] and simulated densities by IAPWS-IF97 [15].

During geological storage of CO_2 under reservoir conditions, an important process will be the convective mixing due to density differences arising from spatially varying amounts of dissolved CO_2 (compare Fig. 3(a)). The simulation of convective mixing requires an accurate determination of the density of the brine containing CO_2, as the latter will influence the prediction of long-term storage conditions for carbon dioxide. The solubility of CO_2 was determined using the method of [21, 22] spanning a parameter range from 298.15 K to 338.15 K, 0 to 500 bar and 0 to 2 mol/kg NaCl, which here is assumed to cover representative reservoir conditions. The results are shown in Fig. 2. It can be seen, that fluid density increases with pressure and NaCl content and decreases with temperature. For high pressures, the curves obtained are parallel to each other, indicating a linear dependence on the reservoir pressure.

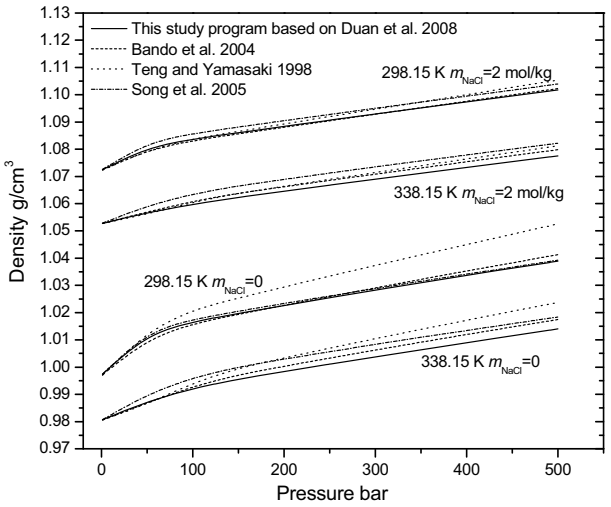

Figure 2. Calculated densities of aqueous CO_2 saturated fluid varying with pressure at given temperature conditions and comparison with previous models [14, 25, 26].

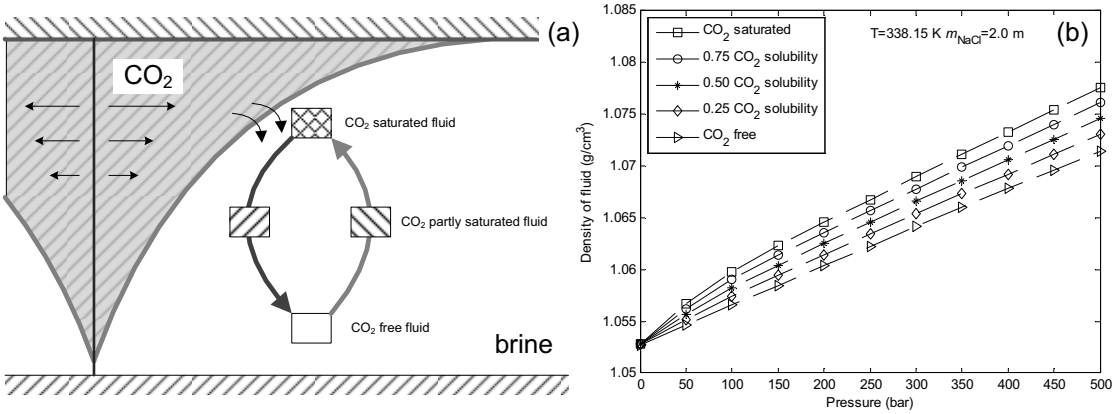

Figure 3. (a) Scenario for convective mixing due to spatial differences in the dissolved amount of CO_2; (b) brine density for 338.15 K and m_{NaCl} of 2 mol/kg for different CO_2 saturations with respect to the solubility limit.

Fig. 3b shows the calculated densities of the formation brine for varying saturation states with respect to a CO_2 phase. It can be seen, that density differences of about 0.005 g/cm³ can arise from different solution contents of CO_2. The effect is more pronounced for higher pressures.

The last example demonstrates how for closed system conditions a temperature increase will lead to a pressure increase, if the volume is constant. In this setting, the isovolumetric pressure at variable temperature conditions has to be determined. For this, an iteration has to be included for the brine pressure. Using initial conditions of 298.15 K, 200 bar, and molalities of NaCl and CO_2 of 2.0 and 0.6 mol/kg, respectively, the reservoir brine density is determined. Then the temperature is increased to 348.15 K under isovolumetric conditions. The change of the total system pressure is shown in Fig. 4. It can be seen, that a strong effect of the heating of the reservoir fluid on the pressure is induced, raising the pressure from the initial 200 bar to more than 900 bar.

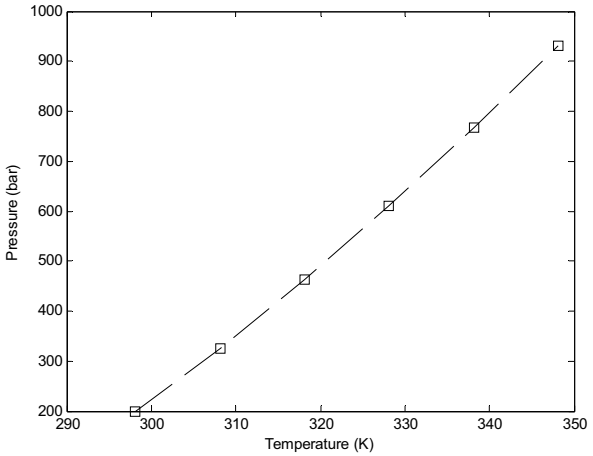

Figure 4. Calculated isovolumetric pressure of the aqueous CO_2 fluid with increasing temperatures.

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